Host–Guest Properties of the Aromatic Propellene 1,4-Bis(pyrazol-1′-yl)-2,3,5,6-tetrakis(3″,5″-dimethylpyrazol-1″-yl)benzene

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Abstract. The structures of 1,4-bis(pyrazol-1′-yl)-2,3,5,6-tetrakis(3″,5″-dimethylpyrazol-1″-yl) benzene **1**, its monohydrate, **1a**, four 1 : 2 host : guest complexes, **1b**–**1e** (acetic, propionic, pentanoic, and (±)-2-methyl butyric acids) and a di-picrate salt, **1f**, have been determined by X-Ray analysis. In all complexes, in the salt and in the monohydrate compound, the host molecules are hydrogen bonded to two centrosymmetric related guests and to the water molecule which is disordered over two positions to mimic the inclusion complexes. In all compounds, the host exhibits C_i symmetry having the lone pair on the N(2) atom of each pyrazole pointing alternately upwards (*u*) and downwards (*d*) from the benzene ring. ^{1}H and ^{13}C NMR spectra of the free host **1** and of the complexes are consistent with the *ududud* conformation and the stoicheiometry of the inclusion compounds.

1. Introduction

We have coined the name aromatic propellenes to describe a series of compounds (Scheme 1) of general formulae $Ar_nAr'_m\Sigma$, in which heteroaromatic rings (Ar or/and Ar′ azoles) are directly linked to a central ring: compounds **1**–**4**: Σ = benzene, $m = 6-n$ and compound **5**: Σ = pyridine, $m = 5-n$. They are interesting for their: (i) conformational aspects which we have studied in depth in previous papers

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[1–5], and (ii) host-guest properties described in this paper. With regard to point (ii), the studied compounds are related to MacNicol's "Hexa-Host" [6], Vögtle and Weber's "Octopus" [7] and to Toda's "Hexa-Pedals" [8] compounds that belong to Ar_6-benzene type with R = others (often a CC triple bond or a O—R′/S—R′ substituent).
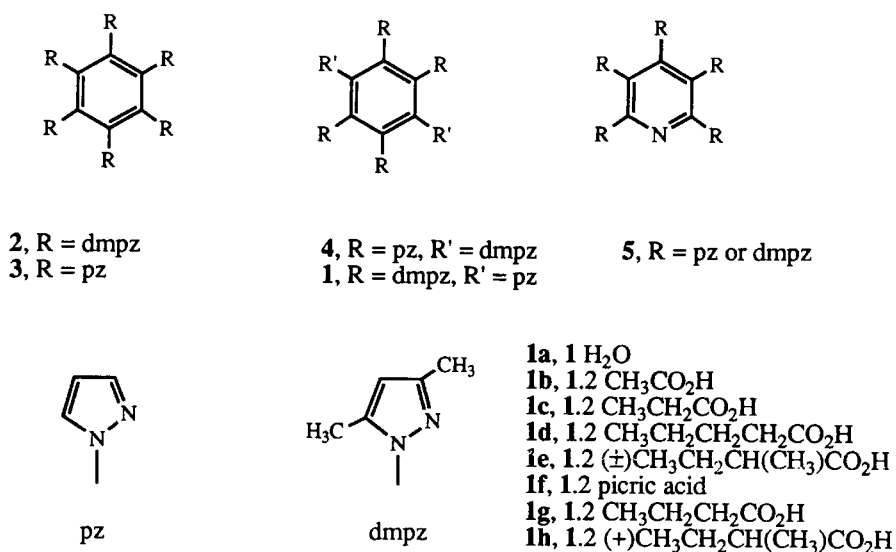
We have summarized the two situations where the periphery is composed of aromatic rings directly joined to the central unit. Gielen and Willen have studied the conformational behaviour of the benzene derivatives with R = *o*-methyl and *o*-methoxybenzene [9, 10], while Müllen has prepared terphenylyl and quater-phenylyl derivatives [11]. Bart discussed the hexaphenylbenzene [12] and Gust the bis(hexaphenylbenzene) anisole clathrate [13]. Henrie described the hexapyrazolylbenzenes [14] and Weiss prepared the first-ever per(onio) substituted benzene [15]. Together with these compounds, the structure of hexapyrrolylbenzene [16] and hexa(pyrazol-1-ylmethyl)benzene [17] have recently been described although in the last compound, the pyrazole rings are not directly linked to a benzene ring. Poly(pyrazol-1-yl)benzenes are extremely interesting ligands in coordination chemistry [17].

We present here our results on the inclusion properties of the title compound, **1**, $Ar_2Ar'_4\Sigma$, where the central core, Σ (with the experimental conditions described elsewhere [1–4, 18]) is benzene and Ar and Ar′ are pyrazole and 3,5-dimethylpyrazole rings respectively directly linked to the propeller core. It is worthy of mention that none of the equally substituted hexakisazolylbenzenes, with R = pyrazole or 3,5-dimethylpyrazole (compounds **2** and **3** respectively in Scheme 1) form inclusion complexes [1, 2]. Only compound **4** cocrystallizes with dimers of acetic acid which only interacts weakly with the host [3].

2. Experimental

2.1. SYNTHESIS

Melting points were obtained on a hot stage microscope and are uncorrected. ^{1}H- and ^{13}C-NMR (solution and CPMAS in ppm from Me_4Si) have been obtained using *Bruker-AC-200* and *Bruker-AM-300* instruments with the experimental conditions described elsewhere [1–4, 18]. 3,5-Dimethylpyrazole (23.67 mmol) in 20 mL of anhydrous THF was placed in a three-necked round-bottomed flask provided with a reflux refrigerator, argon atmosphere and magnetic stirring. To this solution, 23.67 mmol of NaH (60% oil dispersion) were added in small portions and the reaction mixture was heated at 65 °C for 1 h. After cooling, 5.92 mmol of 1,4-bis(pyrazol-1′-yl)-2,3,5,6-tetrafluorobenzene were added and the mixture was heated under reflux for 6 h. A white precipitate of 1,4-bis(pyrazol-1′-yl)-2,3,5,6-tetrakis (3″,5″-dimethylpyrazol-1″-yl)benzene **1** was formed, which after filtration was rinsed first with 20 mL of water and then with 20 mL of THF, yield 92%, R_f = 0.46 (dichloromethane/ethanol 95:5), m.p. = 280 °C (from dichloromethane-hexane) (**1**). The samples recrystallized from ethanol (**1a**), acetic
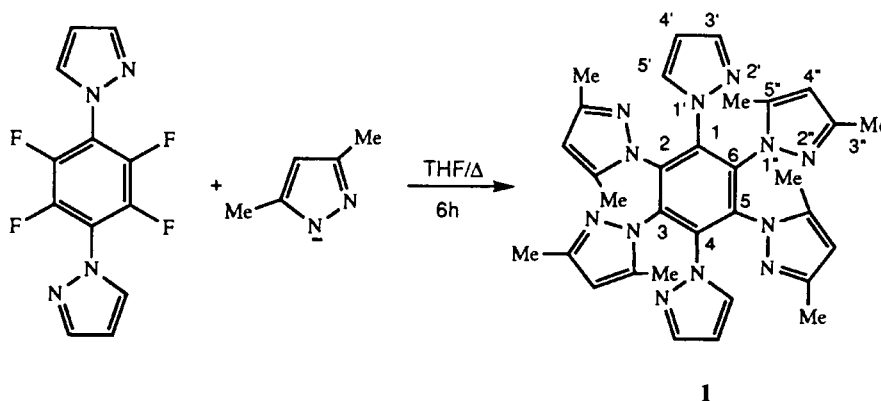
Scheme 1.

2, R = dmpz
3, R = pz

4, R = pz, R' = dmpz
1, R = dmpz, R' = pz

5, R = pz or dmpz

pz

dmpz

1a, 1 H_2O
1b, 1.2 CH_3CO_2H
1c, 1.2 $CH_3CH_2CO_2H$
1d, 1.2 $CH_3CH_2CH_2CH_2CO_2H$
1e, 1.2 ($\pm$)$CH_3CH_2CH(CH_3)CO_2H$
1f, 1.2 picric acid
1g, 1.2 $CH_3CH_2CH_2CO_2H$
1h, 1.2 (+)$CH_3CH_2CH(CH_3)CO_2H$

acid (**1b**), propionic acid (**1c**), pentanoic acid (**1d**), ($\pm$)-2-methylbutyric acid (**1e**), butyric acid (**1g**) and (+)-2-methylbutyric acid (**1h**) showed the same melting point. In the case of the picrate (**1f**) small yellow drops appeared at 185 °C, but the final melting point was again of 281 °C. For **1a** IR (KBr) from ethanol, ν (cm^{-1}): 3525, 2915, 1555, 1525, 1495, 1395, 1345, 1320, 1200, 1120, 1090, 1045, 1035, 1020, 975, 940, 915, 885, 800, 785, 755, 665, 655, 645, 630, 615. MS, m/z (relative intensity,%): 587 (M$^{+\cdot}$ + 1, 26), 586 (M$^{+\cdot}$, 75), 571 (26), 531 (11), 519 (23), 518 (15), 491 (11), 293 (12), 97 (12), 96 (15), 95 (33), 82 (19), 81 (14), 80 (19), 70 (11), 69 (13), 68 (15), 67 (18), 66 (21), 65 (21), 55 (18), 54 (16), 53 (14), 52 (10), 42 (100). Elemental Analysis: calculated for $C_{32}H_{34}N_{12}.H_2O$, C 63.56, H 6.00, N 27.79; found C 63.33, H 5.83, N 27.46%.

2.2. X-RAY STRUCTURE DETERMINATION

Crystal data and experimental details are shown in Table I. Crystals of the butyric acid complex (**1g**) (a = 15.161(3), b = 15.040(2), c = 9.843(2) Å, α = 101.82(2), β = 101.25(1), γ = 92.05(2)°, P-1) appear to be pseudoisomorphous to those of the pentanoic acid complex (**1d**) so that the crystal structure determination was not undertaken. Crystals of the hexanoic acid complex were too unstable, even inside a Lindeman capillary, to carry out the preliminary study. Data for (**1d**) were collected at 200 K using an Oxford Cryostream device [19] and the stated temperature was measured continuously during data collection. Two standard reflexions were monitored every 90 minutes. No variation was observed except in **1e** (18% decay). The structures were solved by direct methods [20] and refined by least-squares procedures on Fo. In all compounds, the host is located on inversion centers, hence

Scheme 2.

the asymmetric unit in **1b** and **1d** is constituted by two independent half molecules and a half in the remaining compounds. The water molecule which is located near an inversion center $[O \cdots O(1 - x, 1 - y, 1 - x) = 2.241(6)$ Å] has a site-occupation factor of 0.50. The nitro group at C(46) in **1f** was also disordered over two positions, **A** and **B**, modeled with occupation factors of 0.85(1) and 0.15(1) respectively. All hydrogens were obtained from difference Fourier synthesis and included and refined isotropically in the last cycles except those of the guest in **1c** and **1e.** The atomic scattering factors were taken from the *International Tables for X-Ray Crystallography*, Vol. IV [21]. The calculations were carried out with the XTAL3.2 System [22], PESOS [23] and PARST [24] set of programs running on a DEC3000-300X workstation.

3. Results and Discussion

3.1. SYNTHESIS

The synthesis of 1,4-bis(pyrazol-1′-yl)-2,3,5,6-tetrakis(3″,5″-dimethylpyrazol-1″-yl) benzene **1**, has been achieved by the reaction of 1,4-bis(pyrazol-1′-yl)-2,3,5,6-tetrafluorobenzene [18] with the 3,5-dimethylpyrazole anion in a 1 : 4 molar ratio in 92% yield (Scheme 2).

3.2. X-RAY CRYSTALLOGRAPHIC STUDY

3.2.1. *Molecular Structure*

The structural details of the parent compound (**1**), its monohydrate (**1a**), four 1 : 2 host:guest complexes (**1b–1e**) and a di-picrate salt (**1f**) are supplied in Table II (pz and dmpz are pyrazole and 3,5-dimethylpyrazole hereinafter) according to the atom labelling scheme, common for all compounds (Figure 1). In the propeller molecule, bond lengths and angles are comparable to those observed in other structures

Table I. Crystal analysis parameters at room temperature except in **1d** where the data were collected at 200K

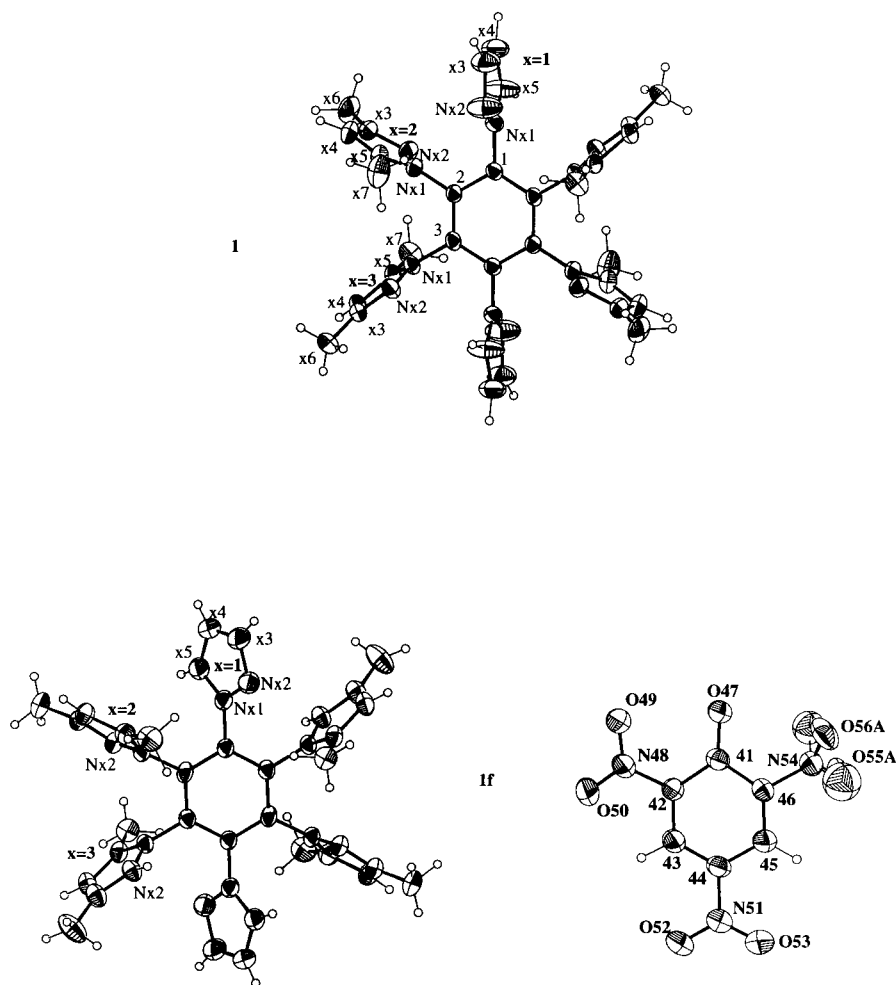|	**1**	**1a**	**1b**	**1c**	**1d**	**1e**	**1f**
Crystal data							
Formula	$C_{32}H_{34}N_{12}$	$\mathbf{1}\cdot H_2O$	$\mathbf{1}\cdot 2C_2H_4O_2$	$\mathbf{1}\cdot 2C_3H_6O_2$	$\mathbf{1}\cdot 2C_5H_{10}O_2$	$\mathbf{1}\cdot 2C_5H_{10}O_2$	$\mathbf{1}^{2+}\cdot 2C_6H_2N_3O_7^-$
Crystal habit	Colourless, prism	Colourless, plate	Colourless, plate	Colourless, prism	Colourless, prism	Colourless, prism	Colourless, prism
Crystal size (mm)	$0.17 \times 0.27 \times 0.10$	$0.10 \times 0.43 \times 0.67$	$0.11 \times 0.33 \times 0.50$	$0.47 \times 0.33 \times 0.17$	$0.67 \times 0.20 \times 0.10$	$0.50 \times 0.33 \times 0.17$	$0.43 \times 0.33 \times 0.10$
Symmetry	Triclinic, P-1	Triclinic, P-1	Triclinic, P-1	Monoclinic, P2$_1$/c	Triclinic, P-1	Triclinic, P-1	Triclinic, P-1
Unit cell determination:							
Least-squares fit from							
reflexions ($\theta < 45°$):	64	76	79	71	113	76	67
Unit cell dimensions (Å,°)	$a = 8.7000(4)$	$a = 8.5896(3)$	$a = 20.8260(20)$	$a = 10.8856(6)$	$a = 15.4523(14)$	$a = 11.4852(6)$	$a = 12.4039(13)$
	$b = 8.9039(9)$	$b = 8.8735(6)$	$b = 10.5951(9)$	$b = 20.2867(17)$	$b = 14.9979(16)$	$b = 10.6900(6)$	$b = 10.9083(16)$
	$c = 11.8088(11)$	$c = 11.4987(7)$	$c = 9.2370(5)$	$c = 9.8256(5)$	$c = 9.9174(6)$	$c = 11.2088(9)$	$c = 9.4254(10)$
	$\alpha = 111.729(8)$	$\alpha = 106.187(6)$	$\alpha = 109.432(5)$	$\alpha = 90$	$\alpha = 100.800(6)$	$\alpha = 63.825(5)$	$\alpha = 98.975(14)$
	$\beta = 1\,12.858(5)$	$\beta = 106.972(4)$	$\beta = 98.412(7)$	$\beta = 112.296(3)$	$\beta = 100.671(5)$	$\beta = 113.078(4)$	$\beta = 80.107(13)$
	$\gamma = 84.065(7)$	$\gamma = 82.832(5)$	$\gamma = 91.719(11)$	$\gamma = 90$	$\gamma = 90.530(9)$	$\gamma = 91.014(5)$	$\gamma = 85.456(13)$
Packing: V(Å^3), Z	782.2(1), 1	804.1(1), 1	1894.6(3), 2	2007.6(2), 2	2216.3(3), 2	1116.0(1), 1	1233.6(3), 1
Dc(g/cm^3), M, F(000)	1.246, 586.7, 310	1.249, 604.72, 320	1.239, 706.81, 748	1.216, 734.9, 780	1.185, 791.0, 844	1.177, 791.0, 422	1.407, 1044.9, 542
μ(cm^{-1})	6.36	6.47	6.92	6.71	6.41	6.36	9.20
Experimental data							
Technique	Four circle diffractometer: Philips PW1100, Bisecting geometry. Graphite oriented monochromator. $\omega/2\theta$ scans.						
	Detector apertures $1 \times 1°$. 1 min./reflex. CuKα. $\theta_{max} = 65°$. Scan width $= 1.5°$. 2 Standard reflexions every 90 minutes. No variation						
Number of reflexions:							
Independent	2659	2739	6472	3425	7425	3826	4035
Observed ($2\sigma(I)$ criterion)	2212	2599	4230	2023	4732	2590	2308
Solution and refinement:							
Solution				Direct methods: Sir92			
Refinement:							
Least-squares on Fo				Full matrix			
Secondary extinction ($\times 10^4$)	–	–	–	0.35(6)	0.52(7)	0.24(3)	0.66(6)
Parameters:							
Number of variables	267	284	637	313	740	327	433
Degrees of freedom	1945	2315	3593	1710	3992	2263	1875
Ratio of freedom	8.29	9.15	6.64	6.46	6.40	7.92	5.33
Final shift/error	0.019	0.014	0.023	0.001	0.012	0.016	0.010
H atoms				From difference synthesis			
Weighting-scheme				Empirical as to give no trends in $\langle\omega\Delta^2 F\rangle$ vs. $\langle|\text{Fobs}|\rangle$ and $\langle\sin\theta/\lambda\rangle$			
Max. thermal value							
Uii component:	U11[C(15)]	U33[O(101)]	U22[O(102)Mol.1]	U11[C(104)]	U22[O(102)Mol.1]	U11[C(103)]	U22[O(50)]
Uii value (Å^2):	0.165(4)	0.108(3)	0.198(5)	0.342(20)	0.082(2)	0.260(14)	0.212(6)
Final ΔF peaks (eÅ^{-3})	0.20	0.22	0.28	0.59	0.39	0.58	0.57
Final R and Rw	0.055, 0.062	0.051, 0.056	0.057, 0.063	0.070, 0.087	0.060, 0.062	0.076, 0.086	0.067, 0.076

Figure 1. Ortep [22] views of **1** and the ions of **1f** displaying the labelling scheme. Ellipsoids are drawn at the 30% probability level.

reported to date [1–3]. In **1f**, two out of four dmpz rings have acquired additional protons from two picric acid molecules and hence the propeller molecule exists as a divalent cation. In the dmpz ring of **1f** where the protonation occurs, the endocyclic bond distances and angles reveal small but significant differences. The general tendency is to become more symmetric with the shortening of the N(31)–N(32) bond and the opening of the angle at the charged N(32).

In the picrate anion, the disordered nitro group with the highest occupancy factor is twisted by 54.9(7)° while the other two remain almost within the plane of the central core (Table IIb). Strong angular deformations, mainly at C(41) and C(42), are notable. The non additivity parameter [NAP = Σ ($\Phi_{i,exp} - \Phi_{i,cal}$)] proposed by Krygowsky [25] was computed ($\Phi_{i,exp}$ and $\Phi_{i,cal}$ being the experimental and

Table IIa. Selected geometrical parameters (Å, °)

Host:	1			1a		
	x = 1	x = 2	x = 3	x = 1	x = 2	x = 3
N(x1)–N(x2)	1.322(4)	1.374(4)	1.376(3)	1.354(2)	1.368(2)	1.369(2)
N(x1)–C(x5)	1.323(7)	1.345(3)	1.354(4)	1.356(2)	1.359(2)	1.357(2)
N(x2)–C(x3)	1.329(6)	1.323(3)	1.320(3)	1.326(2)	1.328(2)	1.329(2)
C(x3)–C(x4)	1.314(8)	1.391(5)	1.394(5)	1.388(2)	1.398(3)	1.399(3)
C(x4)–C(x5)	1.354(5)	1.369(5)	1.372(4)	1.361(3)	1.366(2)	1.376(3)
N(x2)–N(x1)–C(x5)	110.4(3)	112.8(2)	113.0(2)	112.3(1)	113.0(1)	113.0(1)
N(x1)–N(x2)–C(x3)	104.2(3)	103.8(2)	104.1(2)	103.8(1)	103.5(1)	103.9(1)
N(x2)–C(x3)–C(x4)	112.9(4)	111.5(2)	111.1(2)	112.4(2)	111.9(2)	111.6(2)
C(x3)–C(x4)–C(x5)	104.5(4)	106.5(3)	107.2(2)	105.2(2)	106.1(2)	106.3(2)
N(x1)–C(x5)–C(x4)	108.0(4)	105.5(2)	104.6(2)	106.4(2)	105.5(1)	105.3(1)
N(x2)–N(x1)–C(x)–C(x-1)	88.1(3)	−88.0(3)	104.8(3)	58.5(2)	−103.9(2)	96.7(2)

Host: 1b	Mol. 1			Mol. 2		
	x = 1	x = 2	x = 3	x = 1	x = 2	x = 3
N(x1)–N(x2)	1.362(5)	1.375(3)	1.360(3)	1.354(4)	1.369(3)	1.369(3)
N(x1)–C(x5)	1.346(4)	1.360(4)	1.359(5)	1.347(4)	1.358(4)	1.361(4)
N(x2)–C(x3)	1.328(7)	1.329(4)	1.334(6)	1.321(6)	1.328(4)	1.327(5)
C(x3)–C(x4)	1.375(8)	1.397(5)	1.394(6)	1.367(6)	1.394(4)	1.389(6)
C(x4)–C(x5)	1.345(9)	1.359(5)	1.369(5)	1.351(7)	1.369(5)	1.363(5)
N(x2)–N(x1)–C(x5)	112.2(3)	112.4(3)	112.7(3)	111.5(3)	112.1(2)	112.9(3)
N(x1)–N(x2)–C(x3)	102.7(4)	103.7(3)	104.6(3)	103.4(3)	104.9(2)	103.7(3)
N(x2)–C(x3)–C(x4)	112.9(5)	111.5(3)	110.6(4)	113.2(4)	110.6(3)	111.5(4)
C(x3)–C(x4)–C(x5)	105.3(5)	106.6(3)	107.0(4)	104.7(4)	107.0(3)	107.0(4)
N(x1)–C(x5)–C(x4)	106.9(4)	105.7(3)	105.2(3)	107.3(3)	105.4(3)	104.9(3)
N(x2)–N(x1)–C(x)–C(x − 1)	61.5(3)	−94.7(3)	95.8(3)	119.2(3)	−76.7(4)	81.3(4)

Host:	1c			1e		
	x = 1	x = 2	x = 3	x = 1	x = 2	x = 3
N(x1)–N(x2)	1.354(6)	1.365(5)	1.364(4)	1.361(6)	1.376(5)	1.360(4)
N(x1)–C(x5)	1.336(6)	1.358(6)	1.352(6)	1.335(5)	1.351(6)	1.359(6)
N(x2)–C(x3)	1.319(9)	1.332(6)	1.328(7)	1.320(7)	1.320(8)	1.331(7)
C(x3)–C(x4)	1.353(9)	1.389(8)	1.380(7)	1.357(9)	1.380(7)	1.392(5)
C(x4)–C(x5)	1.356(11)	1.360(6)	1.363(8)	1.350(9)	1.371(9)	1.369(7)
N(x2)–N(x1)–C(x5)	111.4(4)	112.8(4)	112.6(4)	111.3(4)	112.2(4)	112.6(3)
N(x1)–N(x2)–C(x3)	103.6(5)	103.6(4)	104.0(4)	103.0(5)	104.5(4)	104.6(4)
N(x2)–C(x3)–C(x4)	112.7(7)	111.4(4)	111.1(5)	113.3(6)	110.9(6)	110.8(4)
C(x3)–C(x4)–C(x5)	105.4(7)	106.7(5)	107.1(5)	104.8(6)	107.5(5)	106.9(4)
N(x1)–C(x5)–C(x4)	106.9(5)	105.4(4)	105.2(4)	107.5(5)	104.9(5)	105.2(4)
N(x2)–N(x1)–C(x)–C(x − 1)	64.7(5)	−99.2(5)	94.7(5)	60.2(5)	−96.9(5)	93.3(5)

Table IIa. Continued

Host: 1d	Mol. 1				Mol. 2		
	x = 1	x = 2	x = 3		x = 1	x = 2	x = 3
N(x1)-N(x2)	1.349(4)	1.378(4)	1.379(4)		1.353(4)	1.376(5)	1.385(4)
N(x1)-C(x5)	1.359(5)	1.375(5)	1.352(4)		1.368(5)	1.363(4)	1.354(5)
N(x2)-C(x3)	1.340(6)	1.338(5)	1.328(4)		1.338(5)	1.339(5)	1.345(5)
C(x3)-C(x4)	1.396(5)	1.410(5)	1.417(5)		1.393(7)	1.408(6)	1.400(6)
C(x4)-C(x5)	1.363(6)	1.373(5)	1.380(5)		1.363(5)	1.386(6)	1.381(5)
N(x2)-N(x1)-C(x5)	112.2(3)	112.8(3)	112.7(3)		112.3(3)	112.6(3)	111.9(3)
N(x1)-N(x2)-C(x3)	104.0(3)	103.4(3)	105.0(3)		103.3(3)	104.3(3)	104.5(3)
N(x2)-C(x3)-C(x4)	112.1(4)	112.3(4)	110.2(3)		113.0(4)	111.4(3)	110.8(3)
C(x3)-C(x4)-C(x5)	104.7(4)	105.8(4)	106.7(3)		104.6(4)	105.9(3)	106.5(3)
N(x1)-C(x5)-C(x4)	107.1(3)	105.8(3)	105.4(3)		106.9(3)	105.8(3)	106.3(3)
N(x2)-N(x1)-C(x)-C(x-1)	54.8(4)	−109.6(4)	89.5(4)		60.0(4)	−105.7(4)	93.8(4)

Host:	1f				1f		
	x = 1	x = 2	x = 3		x = 1	x = 2	x = 3
N(x1)–N(x2)	1.370(6)	1.373(5)	1.350(5)	N(x2)–N(x1)–C(x5)	113.4(4)	112.3(4)	109.9(4)
N(x1)–C(x5)	1.345(8)	1.370(6)	1.358(6)	N(x1)–N(x2)–C(x3)	101.8(4)	104.5(4)	108.2(4)
N(x2)–C(x3)	1.335(9)	1.332(7)	1.341(7)	N(x2)–C(x3)–C(x4)	113.1(7)	110.4(5)	107.6(4)
C(x3)–C(x4)	1.350(11)	1.400(8)	1.374(7)	C(x3)–C(x4)–C(x5)	106.8(6)	107.7(5)	108.5(5)
C(x4)–C(x5)	1.361(10)	1.359(8)	1.377(7)	N(x1)–C(x5)–C(x4)	105.0(6)	105.0(4)	105.7(4)
N(x2)–N(x1)–C(x)–C(x − 1)	51.3(5)	−109.0(5)	101.9(5)				

Table IIb. Selected geometrical parameters for the picrate anion (Å, °)

C(41)–C(42)	1.433(6)	C(42)–C(43)	1.374(7)	C(43)–C(44)	1.364(8)
C(44)–C(45)	1.394(7)	C(45)–C(46)	1.352(6)	C(41)–C(46)	1.435(7)
C(41)–O(47)	1.261(5)	C(42)–N(48)	1.445(8)	C(44)–N(51)	1.452(7)
C(46)–N(54)	1.466(6)	N(48)–O(49)	1.209(7)	N(48)–O(50)	1.218(8)
N(51)–O(52)	1.210(7)	N(51)–O(53)	1.208(8)	N(54)–O(55A)	1.235(8)
N(54)–O(56A)	1.200(8)	N(54)–O(55B)	1.18(4)	N(54)–O(56B)	1.13(7)
C(42)–C(41)–C(46)	112.0(4)	C(41)–C(42)-C(43)	123.0(5)	C(42)-C(43)-C(44)	120.3(5)
C(43)–C(44)–C(45)	120.8(5)	C(44)–C(45)-C(46)	118.0(5)	C(41)-C(46)-C(45)	125.7(5)
C(46)–C(41)–O(47)	121.4(5)	C(42)–C(41)-O(47)	126.5(4)	C(41)-C(42)-N(48)	120.9(4)
C(43)–C(42)–N(48)	116.1(5)	C(43)–C(44)-N(51)	120.1(5)	C(45)-C(44)-N(51)	119.1(5)
C(45)–C(46)–N(54)	117.1(4)	C(41)–C(46)-N(54)	117.2(4)		
C(41)–C(42)–N(48)–O(49)	−12.0(8)			C(43)–C(44)-N(51)–O(52)	7.3(8)
C(45)–C(46)–N(54)–O(55A)	54.9(7)			C(45)–C(46)–N(54)–O(56B)	−40.9(34)

calculated endoclic angles after applying the corrections due to substituents [26]) in order to ascertain whether the endo and exocyclic deformations due to both steric and electronic consequences of the replacement of the H by O⁻ and the nitro groups may be operating here. The value of NAP = 13.5(14)° suggests a strong repulsive interaction between the O⁻ and the nitro group at C(42) with an increase of the exocyclic O(47)—C(41)—C(42) and N(48)—C(42)—C(41) angles with respect to O(47)—C(41)—C(46) and N(48)—C(42)—C(43).

In all cases, the conformation of the host can be described as *ududud* [5] since the lone pairs on atom N(2) in the pz and dmpz rings are alternatively oriented to one side (*u*) and to the other (*d*) of the benzene ring. The dmpz rings are roughly perpendicular to this basal ring while the pz ones subtend angles of approximately 60° with the exception of compound **1** (Table II and Figure 2). The twist of the pyrazole rings is analogous to that shown by the hexaphenylbenzene compound [12] (64.3–69.1° range) although the bis(hexaphenylbenzene) anisole clathrate [13] presents torsion angles in a wider range (67.1–85.3°). As in the present study, the smallest rings, pyrrole or pyrazole, tend to be as coplanar as possible with the central core: a range of 48–69° in hexa(pyrrol-1-yl)benzene [16] and a range of 72.7–89.2° in the hexa(4-dimethylamino-1-pyridinium)benzene hexacation [15].

In all these series of hexakisazolylbenzenes (Scheme 1) only compound **3** (hexakis(pyrazol-1-yl)benzene [2]) and compound **4** (1,2,4,5-tetrakis(pyrazol-1′-yl)-3,6-bis(3″,5″-dimethyl pyrazol-1′-yl)benzene [3]) present polymorphic structures. In **3**, two different conformers, *ududud* and *udduud* (8.37 kJ mol⁻¹ less stable), are observed, while in **4**, the molecules present the same *up-down* conformation (*ududud*).

For compound **1**, the N(*x*2)—N(*x*1)—C(x)—C(*x*−1) torsion angles, heats of formation and differences in energy relative to the absolute minimum for the
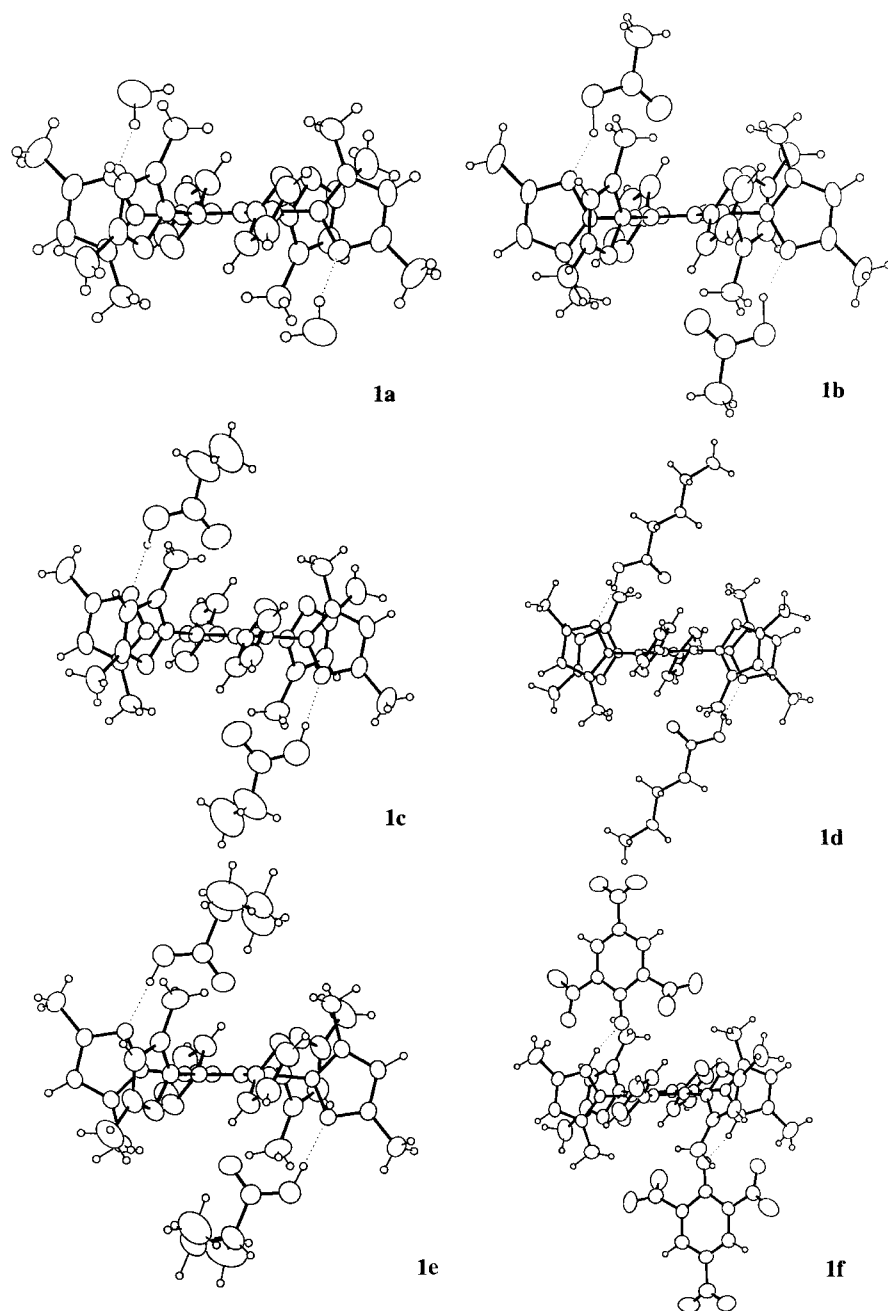
Figure 2. A view parallel to the benzene ring showing the conformation of the host and the hydrogen bonding between the host and the guests (**1a–1e**) and between the cation and the picrate anion in **1f**. In **1b** and in **1d** only molecule 1 is represented. Ellipsoids are drawn at the 30% probability level. Dotted lines indicate hydrogen bonds.

main conformers, as calculated by semiempirical methods at AM1 level [27], are gathered in Table III. The *ududud* conformation corresponds to the most stable conformer [5], where two global minima with C_i and C_2 symmetries (1, 1′) were obtained. The torsion angles (not reported so far) displayed for the C_i point group (Table III) are in a fairly good agreement with the experimental value reported in this paper (Table II) with the exception of **1** already mentioned. Taking as starting points the geometry of these two minima (*1, 1′*), two opposite 3,5-dimethylpyrazole rings have been protonated and the geometry of the resulting cation, present in the picrate salt (**1f**), has been optimized. Both cases converge to a centrosymmetric conformation with torsion angles analogous to those found in the crystal structure (Table II).

3.2.2. *Host–guest disposition*

The anion and the guest units including the water molecule adopt a similar disposition with respect to the host as shown by the pseudotorsion angles, the angles between planes and the hydrogen interactions given in Table IV. The carboxylic group is almost coplanar with the dmpz ring to which it is hydrogen bonded (Figure 2). Despite the size of the guest, two dmpz moieties of the host are hydrogen bonded to two centrosymmetrically related molecules through strong O—H$\cdots$N hydrogen interactions [N$\cdots$O: 2.697(4)–2.761(5) Å] strengthened by weaker C—H$\cdots$O=C contacts [C$\cdots$O: 3.558(5)–3.875(7) Å] with the contiguous dmpz ring (Figure 2). The anions in **1f** are linked by N^+—H$\cdots$O$^-$ hydrogen bonds. In contrast to this salt, H-atom transfer does not occur in the inclusion complexes and all the carboxylic H atoms are ordered (the short C—OH distances in some complexes, Table IV, are due to the high displacement parameters).

All the host molecules are situated in a center of symmetry, consequently, in the case of racemic (±)-2-methylbutyric acid (**1e**), both enantiomers are present in the crystal (they are linked to the host). Unfortunately, all our attempts to grow crystals with (+)-2-methylbutyric (**1h**) as a guest only yielded twins.

3.2.3. *Crystal Packing*

A systematic crystallization using a wide range of different solvents, for the hexakisazolylbenzene derivatives, have been carried out. Only 1,2,4,5-tetrakis(pyrazol-1′-yl)-3,6-bis(3″,5″-dimethylpyrazol-1′-yl)benzene [3] co-crystallizes with a dimer of acetic acid, however the present compound forms inclusion complexes with all the solvents used as summarized in Scheme 1.

Excluding those atoms involved in hydrogen bonds, only the approach of the C—H groups to lone pairs on N(x2) or on O(100) and nitro groups falls short of the corresponding sum of van der Waals radii (2.69 and 2.75 Å for H$\cdots$O/N respectively [28]), Table V. Although some of these contacts can be questioned, factors which may have contributed to the intramolecular interactions include the orientation of the pz moiety ($x = 1$) and the sterical hindrance of the methyl

Table III. AM1 calculations of the main conformers: heats of formation (ΔH), differences ($\delta \Delta H$) in kJ mol^{-1}, point groups (P. g.) and torsion angles $\tau_i = N(\times 2) - N(x1) - C(x) - C(x-1)$ (°)
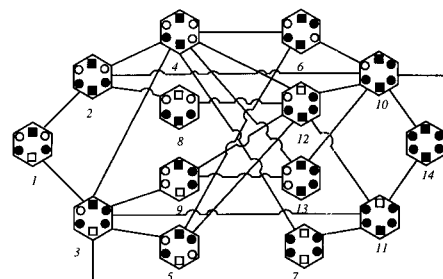
	1	1'	2	3	4	5	6	7	8	9	10	11	12	13	14
ΔH	2008.7	2008.7	2018.4	2018.4	2016.3	2013.8	2014.2	2021.3	2028.0	2024.6	2030.1	2034.7	2027.6	2025.9	2048.5
$\delta \Delta H$	0.0	0.0	9.7	9.7	7.6	5.1	5.5	12.6	19.3	15.9	21.4	26.0	18.9	17.2	39.8
P. g.	Ci	C2	C1	C1	C1	C2	C2	C2	C2	Ci	C1	C1	C1	C1	C2
τ_1	65.5	64.4	63.5	63.9	61.8	63.0	−117.6	63.0	58.3	−118.7	60.1	−118.3	−117.8	61.6	54.5
τ_2	−91.9	−96.0	−96.4	−95.9	−110.0	76.5	−103.6	−110.2	82.0	−105.6	−96.9	75.1	−101.0	−99.2	75.0
τ_3	93.3	83.9	75.1	84.1	−97.9	−102.6	83.2	−98.7	−102.2	−81.0	74.6	65.6	98.2	−76.8	66.1
τ_4	−65.5	−116.3	57.1	−118.0	63.5	−117.0	−117.6	63.0	−120.6	118.7	55.9	54.8	122.5	119.5	54.5
τ_5	91.9	84.3	77.3	−112.2	−96.2	83.5	−103.6	−110.2	−103.9	105.6	74.9	75.6	107.6	103.7	75.0
τ_6	−93.3	−95.8	−96.4	−101.2	77.6	−96.6	83.2	−98.7	75.5	81.0	66.9	67.0	81.8	76.1	66.1

(The torsion angles starting from one pyrazole ring for the divalent cation 1 are: 52.9, −119.0, 91.7, −52.9, 119.0, −91.7; ΔH 3431.3 kJ mol^{-1}).

Table IV. Geometrical parameters (Å, °) characterizing the guest disposition with respect to the host. Π1, Π2 represent the least-squares planes through the pyrazole to which the guest is hydrogen bonded and through the O(100), C(101), O(102) and C(103) atoms respectively. The C—O distances and the geometry of the intermolecular interactions are also given
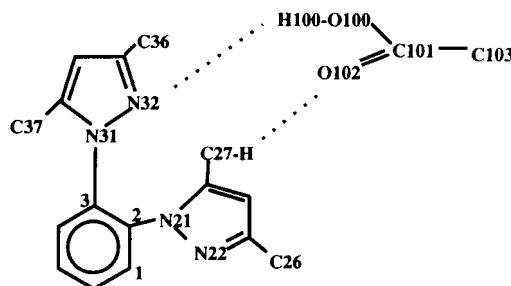
Compound:	1a	1b		1c	1d		1e
		Mol. 1	Mol. 2		Mol. 1	Mol. 2	
C(101)–O(100)	–	1.292(7)	1.289(5)	1.289(10)	1.322(5)	1.339(5)	1.281(12)
C(101)–O(102)	–	1.188(6)	1.188(5)	1.206(11)	1.209(5)	1.199(5)	1.191(9)
C(3)–N(31)–N(32)···O(100)	41.0(2)	−6.2(4)	5.2(5)	−3.7(6)	18.0(5)	7.6(4)	7.3(5)
N(31)–N(32)···O(100)–C(101)	–	22.5(5)	−0.2(6)	16.9(9)	−16.6(5)	−0.5(4)	−8.9(7)
N32···O100–C101–O102	–	3.8(8)	−2.5(7)	4.0(9)	0.0(6)	−2.9(5)	2.0(9)
Π1–Π2	–	21.6(2)	12.8(2)	17.1(2)	14.1(1)	13.4(1)	4.1(2)
O(100)–H(100)···N(32)	1.09(13)	1.17(7)	0.94(5)	0.95(–)	0.92(5)	0.90(6)	0.96(–)
	2.997(4)	2.753(4)	2.697(4)	2.733(6)	2.711(4)	2.741(5)	2.761(5)
	1.94(12)	1.67(9)	1.79(5)	1.78(–)	1.82(5)	1.84(6)	1.81(–)
	162(11)	151(7)	163(5)	180(–)	165(5)	174(6)	176(–)
C(27)–H(273)···O(102)	0.99(3)	0.98(6)	0.97(6)	0.85(12)	1.00(12)	0.90(9)	0.96(10)
	3.558(5)	3.875(7)	3.862(7)	3.761(12)	3.714(7)	3.739(7)	3.603(9)
	2.63(3)	3.32(6)	2.92(6)	3.10(11)	2.72(12)	3.00(10)	2.78(11)
	157(3)	118(4)	164(4)	136(9)	173(9)	140(7)	144(8)

groups, so that the C(15)—H(15)···N(22) contact disappears in **1** where the pz moiety is almost perpendicular to the central ring, 88.1(3)° versus approximately 60° for the remaining *pz* rings (Table II).

For comparison purposes, Figure 3 shows the packing of the molecules for compounds **1** and **1a**. The water molecules are stacked between two propeller molecules and are connected to them by O—H···N hydrogen bonds to form columns along the **a** axis. The crystal structures of **1b** and **1c** are quite similar (Figure 4) while in **1c** the molecules are related by a 2_1 axis, in **1b** there is a pseudo 2_1 axis parallel to **a** [at $y = 0.514(12)$, $z = 0.262(14)$ and 0.499(13) translation] connecting the two independent halves of the host molecules. As can be seen in Figure 4, the differences are due to the location of guest 2 which in **1b** is

Table V. Intra and intermolecular hydrogen interactions (Å, °)

D—H···A	D—H	D···A	H···A	D—H···A
Compound 1				
C(37)–H(373)···N(22)	1.01(7)	3.283(4)	2.46(6)	138(5)
Compound 1a				
C(37)–H(371)···N(22)	0.98(4)	3.293(3)	2.53(5)	135(3)
C(15)–H(15)···N(22)	0.96(3)	3.292(2)	2.77(3)	115(2)
O(100)–H(102)···N(32)(−x + 1, −y + 1, −z + 1)	1.03(10)	3.084(4)	2.32(9)	130(8)
C(36)–H(361)···O(100)	1.01(4)	3.534(5)	2.74(4)	136(4)
Compound 1b: Mol. 1				
C(15)–H(15)···N(22)	0.97(5)	3.208(6)	2.72(5)	112(3)
C(37)–H(373)···N(12)(−x, −y + 1, −z + 1)	0.95(8)	3.421(6)	2.79(8)	125(6)
Compound 1b: Mol. 2				
C(27)–H(271)···N(32)	0.96(6)	3.307(6)	2.55(6)	136(4)
C(37)–H(372)···N(12)(−x + 1, −y + 1, −z)	0.94(5)	3.561(6)	2.75(5)	146(4)
Compound 1c				
C(37)–H(372)···N(22)	1.05(9)	3.405(9)	2.67(9)	128(6)
Compound 1d				
C(37)–H(372)Mol. 1···N(22)Mol.	0.93(9)	3.263(6)	2.64(9)	125(6)
C(14)–H(14)Mol. 1···N(22)Mol. 1(−x, −y, 2 − z)	1.07(6)	3.436(5)	2.67(5)	141(3)
[3pt] C(37)–H(372)Mol. 2···N(22)Mol. 2	1.00(5)	3.348(5)	2.52(5)	141(4)
C(14)–H(14)Mol. 2···N(22)Mol. 2(−x + 1, −y + 1, −z)	1.00(6)	3.525(5)	2.70(6)	140(4)
C(15)–H(15)Mol. 2···O(102)Mol. 2(−x + 1, −y + 1, −z + 1)	0.97(5)	3.399(5)	2.79(4)	122(3)
C(26)–H(262)Mol. 2···O(100)Mol. 2(x, y, z − 1)	0.98(7)	3.593(5)	2.69(7)	154(6)
C(37)–H(371)Mol. 2···N(12)Mol. 1(x + 1, y + 1, z)	0.97(5)	3.583(5)	2.74(5)	145(4)
C(24)–H(24)Mol. 1···O(100)Mol. 2(x, y − 1, z)	1.03(5)	3.399(5)	2.53(4)	142(4)
C(24)–H(24)Mol. 2···O(100)Mol. 1(x, y + 1, z)	1.05(5)	3.424(5)	2.57(5)	138(4)
Compound 1e				
C(37)–H(372)···N(22)	0.90(8)	3.324(8)	2.61(8)	137(7)
C(15)–H(15)···N(22)	0.82(7)	3.229(9)	2.72(8)	122(5)
C(37)–H(373)···N(12)(−x, −y, −z)	0.88(9)	3.415(7)	2.78(7)	131(6)
Compound 1f				
N(32)–H(32)···O(47)	1.03(5)	2.633(5)	1.63(5)	166(5)
C(37)–H(371)···N(22)	0.86(6)	3.268(8)	2.64(6)	131(5)
C(27)–H(272)···N(12)	0.96(7)	3.559(8)	2.73(7)	145(6)
C(27)–H(273)···O(47)	1.09(9)	3.534(9)	2.48(9)	164(6)
N(32)–H(32)···O(49)	1.03(5)	2.876(6)	2.38(5)	108(4)
C(15)–H(15)···O(56A)(−x, −y, −z)	0.89(5)	3.312(8)	2.57(5)	142(4)
C(37)–H(371)···O(55A)(−x, −y, −z)	0.86(6)	3.294(8)	2.72(5)	126(5)
C(14)–H(14)···O(55A)(x, y − 1, z)	0.83(6)	3.359(10)	2.64(6)	146(5)
C(26)–H(262)···O(56A)(x, y − 1, z)	0.89(12)	3.292(11)	2.72(11)	123(8)
C(34)–H(34)···O(49)(−x − 1, −y, −z)	0.93(6)	3.432(7)	2.76(5)	131(4)
C(34)–H(34)···O(50)(−x − 1, −y, −z)	0.93(6)	3.544(8)	2.62(6)	173(4)
C(24)–H(24)···O(50)(−x − 1, −y, −z + 1)	0.97(6)	3.485(7)	2.68(5)	141(5)
C(26)–H(263)···O(53)(x, y − 1, z − 1)	1.09(16)	3.442(12)	2.63(18)	131(11)
C(37)–H(372)···O(53)(x, y − 1, z − 1)	1.06(9)	3.261(9)	2.77(8)	108(5)

Table VI. ^{13}C-NMR data in CDCl$_3$ solution[a] and in the solid state CPMAS[b] of [(pz)$_2$(dmpz)$_4$bz] **1** and its inclusion compounds **1a–1e** (δ in ppm, *J* in Hz). Also the guests signals are given.

| | Benzene ring | | Pyrazole ring | | | 3,5-Dimethylpyrazole ring | | | | |
Comp	C–1/C–4	C–2/C–3	C–3'	C–4'	C–5'	C–3''	C–4''	C–5''	CH$_3$–3''	CH$_3$–5''
1[a]	138.7	136.8	141.1	106.3	131.9	149.8	105.0	143.7	13.3	11.1
			$^1J_{H3'} = 186.2$	$^1J_{H4'} = 178.0$	$^1J_{H5'} = 192.5$		$^1J_{H4}{}^3Me3'' = 173.2$		$^1J = 127.2$	$^1J = 129.3$
			$^2J_{H4'} = 6.0$	$^2J_{H3'} = 10.5$	$^2J_{H4'} = 9.5$		$^3J_{Me''} = 3.2$			
			$^3J_{H5'} = 8.5$	$^2J_{H5'} = 8.7$	$^3J_{H3'} = 4.3$		$^3J_{Me5''} = 3.2$			
1a[b]	139.4	137.1	141.6	103.8	132.3	147.1	106.4	142.8	13.3	11.2
				106.4		149.5			14.1	12.2
						150.9				12.6
1b[b]	140.7	136.8br	140.7	104.9	131.4	147.4	107.3	142.4	13.0	9.7
				106.8			108.1		13.9	12.1
1c[b]	140.6	138.0br	141.1	105.3	132.3	147.1	106.9	142.5	12.6	10.6
						148.7	107.9		14.2	12.6
						149.7				
1g[b]	139.7	139.7	141.7	105.0	131.3	147.2	106.5	141.7	12.9	12.1
				105.1	132.4	148.3	107.6		13.4	
						149.1				
						149.8				
1d[b]	139.2	137.0	141.6	104.4	132.0	147.8	106.2	140.0	12.9	9.4
				105.3		149.0	108.7			11.6
1e[b]	140.3	137.0	141.5	104.5	130.3	148.8	106.1	142.5	13.0	9.3
						148.9			13.6	12.4

Guests	C=O	C—2	C—3	C—4	C—5	C—2'
1b[b]	171.8	20.6				
	172.5	22.1				
1c[b]	175.4	27.8	9.4			
1g[b]	175.0	35.0	17.8	13.9		
1d[b]	173.4	34.4	27.4	23.0	14.7	
	174.2			23.4	15.4	
1e[b]	177.5	40.5	27.3	18.4br		12.4
		39.7				
[c]	183.6	40.9	26.5	16.2		11.4

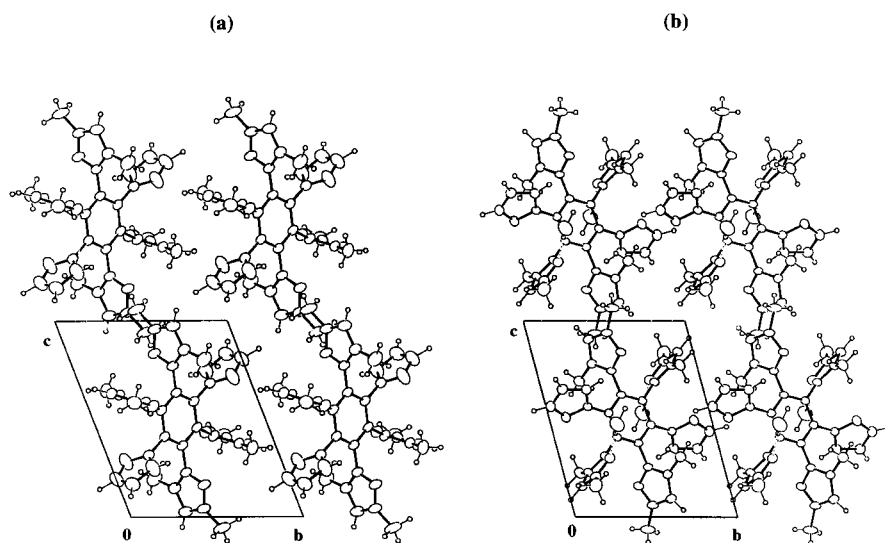[c] ($\pm$)-2-methylbutyric acid in CDCl$_3$.

Figure 3. Crystal packing for **1** (a) and **1a** (b) along the **a** axis.

linked to N(22) instead of N(32) breaking the symmetry. In **1d** (Figure 5), the two independent molecules are linked by C—H···N/O contacts along the [1 1 0] and [1 −1 0] directions respectively. No intermolecular interactions other than van der Waals are observed in the crystal structure of **1e** (Figure 6). In **1f**, apart from the strong N^+—H···O^- hydrogen bond that holds the host and the guest molecules, a three dimensional network of weak C—H···O contacts are observed (Figure 6). In the inclusion complexes, pairs of guests or picrate anions (Figures 4 and 6) are included in the same cavity, except in **1d** (Figure 5) where four guests are allocated in one cavity; all these cavities can be considered prolate in shape although close to a spherical tipped rod [29]. There are no voids in the structures and the total packing coefficients are in the 0.63–0.68 range, extreme values correspond to the propionic acid complex and the picric salt. The lowest and highest local packing coefficients are 0.47 (**1b**, **1c**, **1e**) and 0.57 (**1f**) ($C_k^{all} = V_{molecules}/V_{Unit\ Cell}$, $C_{local} = V_{guest}/V_{hole}$).

3.3. NMR SPECTROSCOPY

3.3.1. ^1H NMR Studies in Solution

The ^{1}H-NMR spectra of inclusion compounds allow determination of the stoichiometry; apart from that, they contain the signals of the host plus those of the guests which are common compounds, and for this reason, these data will be omitted. Host **1** presents the following signals in $CDCl_3$ solution: $\delta 7.29$ (d, H-3′), 6.05 (dd, H4′), 7.32 (d, H-5′) ($J_{3'4'} = 1.9$, $J_{4'5'} = 2.5$ Hz), 5.58 (s, H-4″), 2.02 (s, CH_3-3″) and 1.98 (s, CH_3-5″).

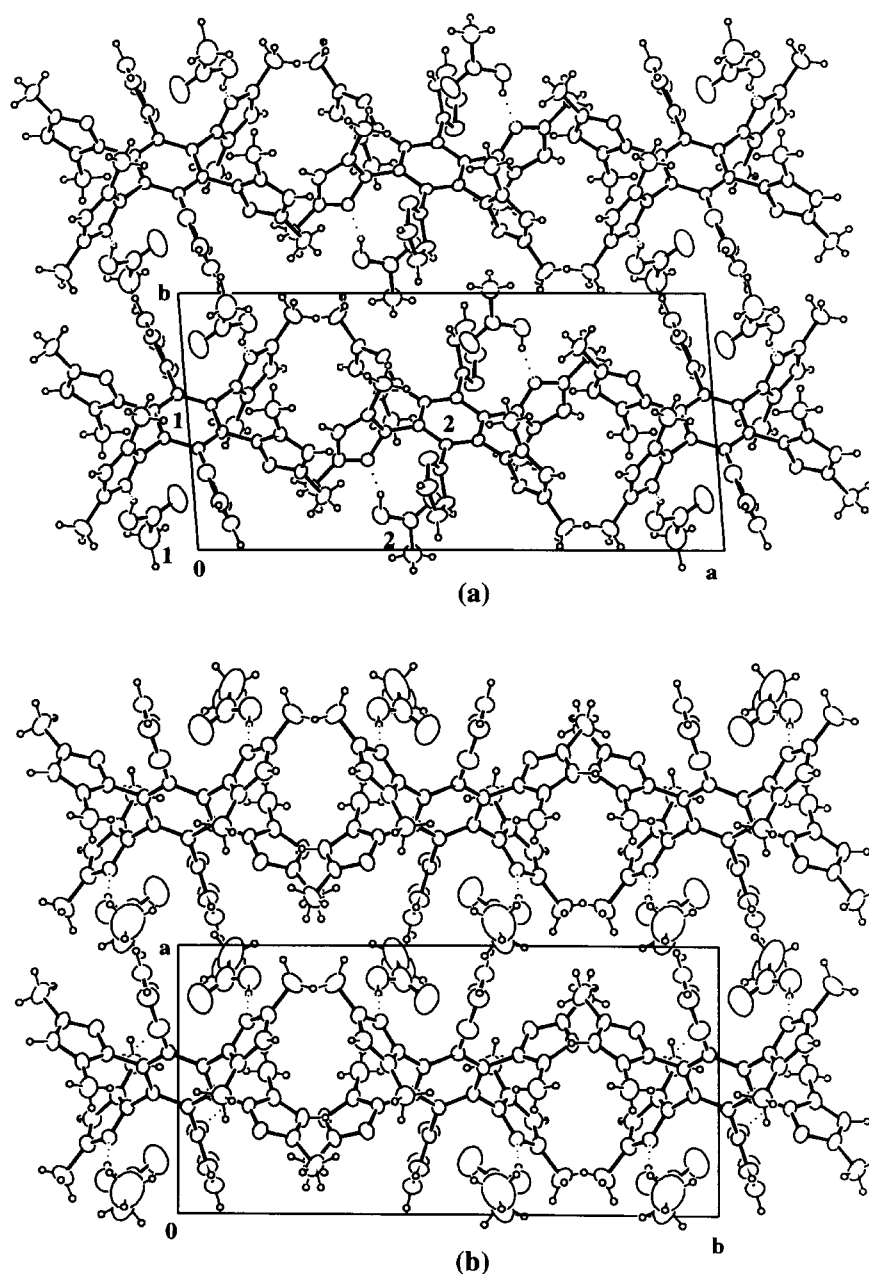*Figure 4.* Crystal packing for **1b** (a) and **1c** (b) along the **c** axis.

Figure 5. Crystal packing for **1d** along the **c** axis.
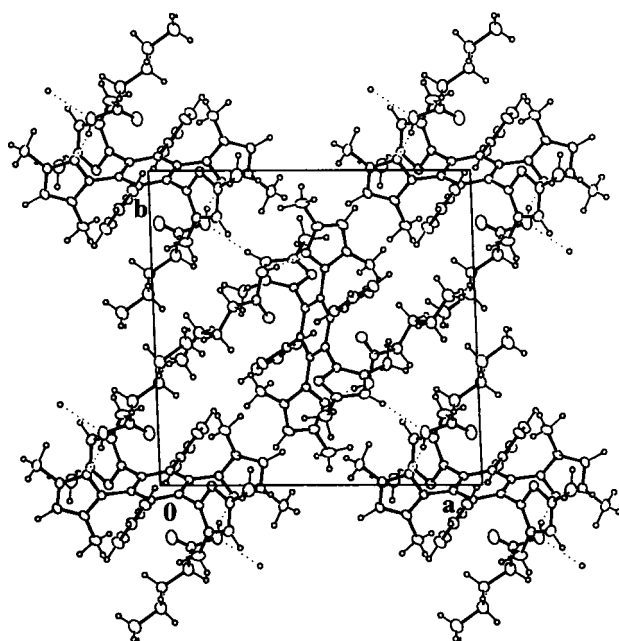

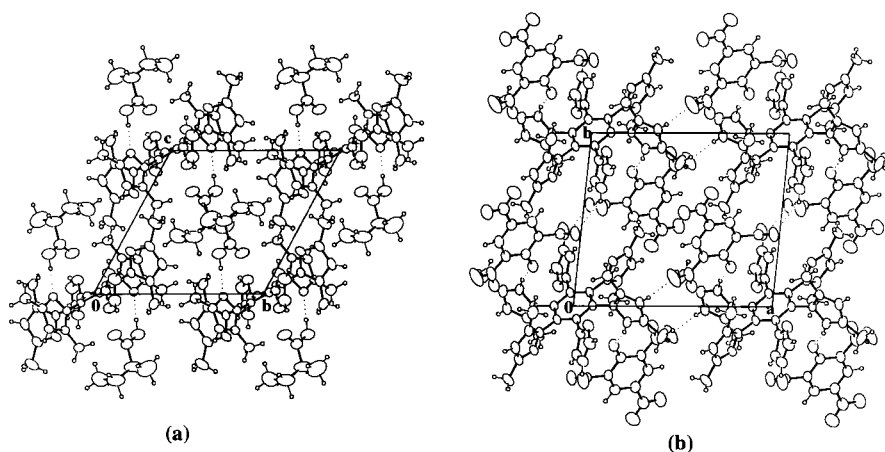**(a)**   **(b)**

Figure 6. Crystal packing for **1e** (a) along the **a** axis and **1f** (b) along the **c** axis.

3.3.2. ^{13}C *Studies in Solution and in the Solid State (CPMAS NMR)*

The simplicity of the ^{13}C NMR spectrum of the free host **1** in CDCl$_3$ solution is consistent with its *ududud* conformation, which remains unaltered in all the complexes. The resolution of the ^{13}C CPMAS spectra of compounds **1–1e** is very high (see, for example, Figure 7), this allows observation of the splitting of several signals (C-4′, C-3″, C-4″ and the methyl groups); these splittings result from dif-
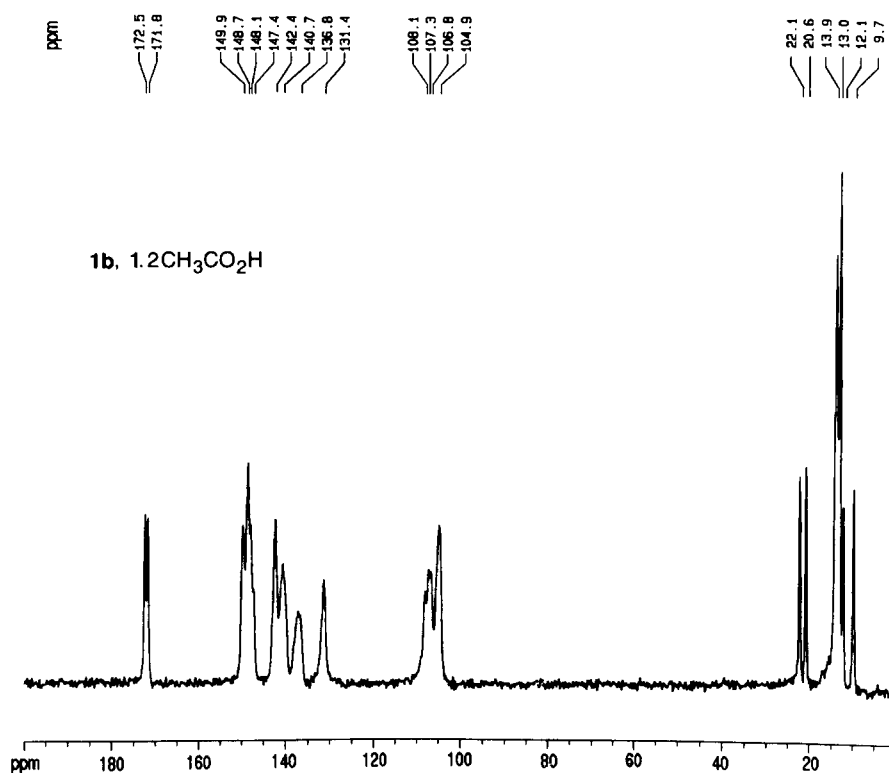
Figure 7. ^{13}C CPMAS spectrum of **1b**: **1**.2CH$_3$CO$_2$H.

ferences in magnetic environments in the solid state (Table VI). The signals of the different guests are clearly observed and the corresponding chemical shifts agree with literature data in solution which were available for all acids apart from ($\pm$)-2-methylbutyric acid (complex **1e**) [30]. The splitting of signals also affects the guests, probably reflecting the 1 : 2 host-guest stoechiometry.

4. Conclusions

We have reported in this paper the host-guest behaviour of 1,4-bis(pyrazol-1$'$-yl)-2,3,5,6-tetrakis(3$''$,5$''$-dimethylpyrazol-1$''$-yl)benzene [(pz)$_2$(dmpz)$_4$bz] **1**. The ability of **1** to form host-guest compounds is due to the presence in its structure of four dmpz substituents, more basic than the pz ones, in an environment less sterically hindered than that of hexakis(3$'$,5$'$-dimethylpyrazol-1$'$-yl)benzene [(dmpz)$_6$bz] **2**.

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